(54) **Process for the production of methanol**

Verfahren zur Herstellung von Methanol

Procédé pour la préparation de méthanol

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EP-A- 0 329 292   **GB-A- 2 179 366**

Description

The present invention relates to a process for the production of methanol, and more specifically to a process for the synthesis of methanol from hydrocarbons with a fluidized bed catalytic reactor.

Methanol is used in large amounts since it is almost free from environmental pollution and easy to transport, and it is demanded to develop an ultra-large scale apparatus capable of producing 5,000 tons/day, 10,000 tons/day or more of methanol.

In recent years, in order to cope with such an ultra-large scale apparatus for producing methanol for use as a fuel, the development of a fluidized bed catalyst reactor is under way. For example, JP-A-60-84142, JP-A-60-122040 and JP-A-60-106534 (corresponding to U. S. Patent 4,666,945) disclose methods for the production of fluid catalysts for the synthesis of methanol. Further, JP-A-63-211246 (corresponding to U. S. Patent 4,956,392) discloses catalysts and reaction conditions for the synthesis of methanol with a fluidized bed.

The largest problem in the development of the above large-scale apparatus for the production of methanol is to increase the capacity of a gas-reforming apparatus for the production of a synthetic gas from hydrocarbons. A conventional steam-reforming apparatus uses the system of externally heating reaction tubes in a reforming furnace, and when the capacity of an apparatus for the production of methanol is increased, the limit of the capacity of the apparatus is 1,500 to 2,000 tons/day.

A method using the combination of a steam-reforming and a partial oxidation is attracting attention as a method of gas reforming with a large-scale apparatus. This method is carried out as follows. A hydrocarbon and steam are mixed and subjected to a primary reforming reaction. Then, oxygen is added, and a partial oxidation and a secondary reforming reaction are carried out. The resultant gas having a high temperature is used as a heat source for the primary reforming reaction. Advantageously, this method requires no external supply of heat, nor does it require a reforming furnace in which reaction tubes are to be externally heated. Therefore, a synthesis gas having a high pressure can be obtained, and the synthesis reaction of the synthesis gas can be directly carried out without increasing the pressure of the synthesis gas with a compressor. Thus, the reforming reaction is carried out under a high pressure, the capacity of the apparatus therefor can be easily increased.

U.S. Patents 4,666,680, 5,112,578 and 5,156,821 disclose specific structures of self heat-exchanger type reactors in which the primary and secondary reforming reactions are carried out.

The reaction for reforming a hydrocarbon with steam is represented by the following reaction schemes.

$$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2 \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$
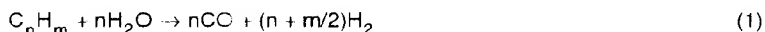
In the development of a large-scale apparatus for the production of methanol, it is desired to improve the energy efficiency, and concerning a gas-reforming apparatus, it is under way to develop a self heat-exchanger type reactor for carrying out the primary reforming reaction and the secondary reforming reaction as described above. For an apparatus for the synthesis of methanol, the development of a fluidized bed catalyst reactor is under way as already described, while the gas flow speed is required to be 0.4 to 0.6 m/second for achieving an optimum fluidization state of a catalyst as described in U.S. Patent 4,956,392. Therefore, the amount of a feed gas to a methanol synthesis reactor is defined, and it is required to decrease the amount of a circulating gas as low as possible. However, when the synthesis gas circulation ratio (amount of circulating gas/amount of synthesis gas) is decreased, the concentration of carbon oxides ($CO + CO_2$) in a gas fed to the methanol synthesis reactor increases, and the temperature in the reactor is liable to increase. As a result, the amount of byproducts such as paraffin increases, and the activity of the catalyst may decrease to a great extent.

In the self heat-exchanger type reactor in which the primary reforming reaction, partial oxidation reaction and secondary reforming reaction are carried out, mainly, hydrogen in a gas from the primary reforming reaction reacts with oxygen to increase the concentration of carbon oxides ($CO + CO_2$) in a synthesis gas. That is, the concentration of carbon oxides ($CO + CO_2$) in the synthesis gas to be fed to a methanol synthesis apparatus increases. The apparatus for the production of methanol comprises a gas-reforming apparatus having a self heat-exchanger type reactor in which the primary reforming reaction, partial oxidation and secondary reforming reaction are carried out and a methanol synthesis apparatus having a fluidized bed catalyst reactor. Therefore, special reaction conditions and improvements in the methanol synthesis process are required for developing a large-scale apparatus for the production of methanol which apparatus has high energy efficiency.

It is an object of the present invention to provide a process for the production of methanol, which exhibits high

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energy efficiency and permits the production of methanol with a large-scale apparatus

It is another object of the present invention to provide a process for the production of methanol, which accomplishes high energy efficiency and comprises a gas reforming step including the steps of primary reforming, partial oxidation and secondary reforming, and a methanol synthesis step using a fluidized bed catalyst reactor, in which the above two steps (gas reforming step and methanol synthesis step) can be carried out with apparatus of which the capacities are increased

According to the present invention there is provided a process for the production of methanol, comprising a primary reforming step of catalytically reacting a hydrocarbon as a raw material with steam, a partial oxidation step of partially oxidizing a gas fed from the above primary reforming step by adding an oxygen gas, a secondary reforming step of catalytically reacting a gas fed from the above partial oxidation step with steam, a step of using a high-temperature gas obtained from the secondary reforming step as a heat source for the primary reforming step a synthesis gas preparation step of separating steam from the gas used as the above heat source to prepare a synthesis gas, and a methanol synthesis step which comprises introducing the synthesis gas into a methanol synthesis reactor with a fluid bed catalyst,

wherein

- a proportion of a gas from the methanol synthesis reactor is re-introduced into the methanol synthesis reactor as a circulating gas together with the synthesis gas;
- a remaining part of the gas from the methanol synthesis reactor is introduced into the primary reforming step as a purge gas together with the hydrocarbon as a raw material; and
- at least one step selected from (a), (b), (c) and (d) is carried out to bring the molar ratio of hydrogen to carbon oxides in a feed gas to be introduced into the methanol synthesis reactor, represented by $[H_2/(2CO + 3CO_2)]$, to from 1.0 to 2.7, and to bring the molar ratio of CO_2/CO in the feed gas to from 0.6 to 1.2:

(a) introducing the synthesis gas into the methanol synthesis reactor after carbon dioxide gas is removed from the synthesis gas;

(b) removing carbon dioxide gas from part of the purge gas, and introducing that part of the purge gas into the methanol synthesis reactor together with the synthesis gas;

(c) cooling the gas obtained from the methanol synthesis step with the heat of evaporation of liquid oxygen to be used in the gas reforming step and/or by low temperature oxygen to be used in the gas reforming step, to divide the gas into a feed gas and crude methanol which can dissolve a large amount of carbon dioxide gas, and feeding the feed gas, as a circulating gas, to the methanol synthesis reactor together with the synthesis gas; and

(d) separating hydrogen from part of the purge gas and feeding the separated hydrogen to the methanol synthesis reactor together with the synthesis gas.

Fig. 1 is a flow chart showing the introduction of a synthesis gas prepared by removing a predetermined amount of carbon dioxide gas with crude methanol to a methanol synthesis reactor

Fig. 2 is a flow chart showing the introduction of a purge gas prepared by removing a predetermined amount of carbon dioxide gas with crude methanol to a methanol synthesis reactor.

Fig. 3 is a flow chart showing the introduction of a gas portion, which is separated from a gas from a methanol synthesis reactor by cooling the gas with the heat of evaporation of liquid oxygen to be used in a gas reforming step and the sensible heat of a low-temperature oxygen gas to be used in the gas reforming step, to a methanol synthesis reactor as a circulating gas together with a synthesis gas.

Fig. 4 is a flow chart showing the introduction of hydrogen separated from part of a purge gas with a pressure swing adsorption (PSA) apparatus to a methanol synthesis reactor.

The present inventors have made diligent studies to overcome the above problems of an apparatus for the production of methanol, which comprises a gas reforming apparatus using a self heat-exchanger type reactor for carrying out the primary reforming reaction, partial oxidation and secondary reforming reaction and a methanol synthesis apparatus using a fluidized bed catalyst reactor. As a result, it has been found that an apparatus for the production of methanol, which can achieve high yields and a high energy efficiency and permits an increase in the capacity of the apparatus, can be obtained by defining the composition of a feed gas to a methanol synthesis reactor

A method of the invention, in which a suitable composition of a feed gas to a methanol synthesis reactor is accomplished with high energy efficiency typically comprises.

a. a primary reforming step of mixing part of the purge gas with the hydrocarbon as a raw material to prepare a mixed gas, adjusting 40 to 80 mol% of the mixed gas to have a molar ratio (S/C) of steam (S) to hydrocarbon (C) of 1 5 to 4 0 and introducing the adjusted mixed gas into the primary reforming step to carry out the primary re-

forming reaction such that outlets of reaction tubes show a pressure of 25 to 95 atmospheric pressure and a temperature of 700 to 800°C,

b. a partial oxidation step of adding oxygen gas in an amount of 0.40 to 0.46 mol per mole of total carbon of hydrocarbon as a raw material to a primary reformed gas and a remainder of the above mixed gas to carry out a partial oxidation, and

c. a step of using a secondary reformed gas obtained from the secondary reforming step as a heat source for the primary reforming step, separating unreacted steam by heat recovery and cooling, and introducing the synthesis gas into the methanol synthesis reactor.

The synthesis gas is typically introduced into the methanol synthesis reactor through a compression step.

For achieving the above composition of a feed gas to the methanol synthesis reactor such that higher energy efficiency can be obtained, the following process may be employed.

1) Carbon dioxide gas is removed from a reformed gas obtained from the gas reforming step or a purge gas from the methanol synthesis step, and the remainder is introduced into the methanol synthesis reactor.

2) The heat of evaporation of liquid oxygen to be used in the gas reforming step and/or the sensible heat of a low-temperature oxygen gas to be used in the gas reforming step is used as a cooling source in the methanol synthesis step.

3) Hydrogen separated from a purge gas from the methanol synthesis step with a PSA (pressure swing adsorption) apparatus is introduced into the methanol synthesis step.

The present invention will be detailed hereinafter.

For bringing the composition of a feed gas to the methanol synthesis reactor using a fluid catalyst into the above range, various factors are to be considered, such as the composition of the synthesis gas to be introduced into the methanol synthesis step, the reaction ratio in the methanol synthesis reactor, the amount ratio of a purge gas from the methanol synthesis step, the amount ratio between the synthesis gas and the circulating gas, and the like, while the composition of the synthesis gas from the gas reforming step is the main factor which affects the composition of the feed gas.

The gas reforming step generally uses a natural gas composed mainly of methane as hydrocarbon as a raw material, while LPG and naphtha are also used in some locations. Further, for improving the unit requirement of the raw material, a purge gas from the methanol synthesis step is also used together with the hydrocarbon. A nickel-containing catalyst is generally used as a steam reforming catalyst, and for avoiding the deactivation of the catalyst, it is required to desulfurize the hydrocarbon as a raw material in advance.

In the present invention, for bringing the composition of a feed gas to the methanol synthesis reactor into the above range such that higher energy efficiency can be obtained, part of a purge gas from the methanol synthesis step can be mixed with hydrocarbon as a raw material, and 40 to 80 % of the mixed gas can be introduced into the primary reforming reaction tubes after the steam/total carbon of raw material molar ratio (S/C) is adjusted to from 1.5 to 4.0. This mixed gas to be introduced into the primary reforming reaction tubes is preferably heated to about 400 to 550°C.

When the amount of mixed gas (mixture of purge gas and hydrocarbon) which bypasses (i.e., the amount of mixed gas fed to the partial oxidation) is too large, the amounts of hydrocarbon as a raw material and steam used in the primary reforming reaction are small, and the amount of hydrogen generated is small. As a result, the stoichiometric ratio between hydrogen and carbon oxides in the feed gas to the methanol synthesis reactor decreases, and the amount of oxygen used for the partial oxidation increases. In the present specification the "stoichiometric ratio" refers to a $[H_2/(2CO + 3CO_2)]$ molar ratio in the feed gas to the methanol synthesis reactor.

When the amount of mixed gas which bypasses is too small, the amount of mixed gas to be fed to the primary reforming reaction is large, and the amounts of hydrocarbon as a raw material and steam are large. As a result, the CO_2/CO molar ratio -(to be referred to as "CO_2 ratio" hereinafter) in the feed gas to the methanol synthesis reactor increases.
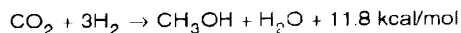
In the steam reforming reaction, the mixed gas of hydrocarbon and steam is indirectly heated through primary reforming reaction tubes to carry out a primary reforming catalytic reaction, such that the outlets of the primary reforming reaction tubes typically show a pressure of 25 to 95 atmospheric pressures and a temperature of 700 to 800°C. The primary reformed gas and a remainder of the mixed gas (of purge gas and hydrocarbon as a raw material) can be introduced into a combustion chamber together with an oxygen gas in an amount of 0.40 to 0.46 mol per mole of total carbon of the hydrocarbon as a raw material to carry out a partial oxidation reaction and a subsequent secondary reforming reaction. The resultant high-temperature reformed gas is subjected to various heat recoveries, and then cooled to form a synthesis gas containing, as effective components, hydrogen, carbon monoxide and carbon dioxide gas.

The primary reformed gas is partially oxidized and then subjected to the secondary reforming reaction. As a result

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the pressure in the gas reforming apparatus is increased, and the power required for a compressor compressing the synthesis gas can be decreased. Therefore, the energy efficiency in the methanol process can be improved. Further the size of the gas reforming apparatus can be decreased since it can be operated at an increased pressure, and the decreased size of the gas reforming apparatus is advantageous for increasing the capacity of the methanol production apparatus.

Further, when the secondary reformed gas is used as a heat source for the primary reforming reaction the difference between the pressure inside the primary reforming reaction tubes and the pressure of the heating gas is small. As a result, a heat-exchanger type reactor can be used, and no externally heated reforming furnace is required. Therefore, a gas reforming apparatus operable at a higher pressure can be employed, and at the same time, it is also facile to cope with an increase in the capacity of the apparatus. Further, when the pressure of the gas reforming apparatus is properly arranged to be higher than the pressure of the methanol synthesis apparatus, no compressor for the synthesis gas is required.

A fluidized bed catalyst reactor is used as the methanol synthesis reactor in which methanol is synthesized from hydrogen, carbon monoxide and carbon dioxide gas according to the following reaction schemes.

$$CO + 2H_2 \rightarrow CH_3OH + 21.6 \text{ kcal/mol}$$

$$CO_2 + H_2 \rightarrow CO + H_2O - 9.8 \text{ kcal/mol}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O + 11.8 \text{ kcal/mol}$$
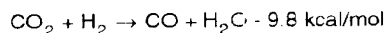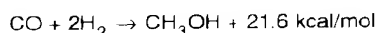
Generally, a copper-containing catalyst is used for the methanol synthesis reaction, and the reaction is carried out at a temperature of 200 to 300°C at a pressure of 60 to 120 atmospheric pressures.

As a fluid catalyst for the methanol synthesis, generally there is used a catalyst prepared by allowing a solid support such as silica, alumina or zirconium to support the catalyst component, and the catalyst has a particle diameter of 1 to 250 μm.

The methanol synthesis uses a fluidized bed catalytic reactor having heat-transfer tubes inside, and the heat of reaction is transmitted to saturated water through the heat-transfer tubes, whereby high-pressure steam having a pressure of 20 to 60 atmospheric pressures, preferably 25 to 55 atmospheric pressures, is recovered.

The high-pressure steam obtained may be used as a steam for the gas reforming step, while it can improve the energy efficiency of the methanol production process when used as a power source for a synthesis gas compressor a synthesis gas circulator or a compressor for hydrocarbon gas as a raw material.

An oxygen separating apparatus for preparation of oxygen for the partial oxidation uses a cryogenic separation method, and the oxygen gas used for the partial oxidation generally has a purity of at least 98 %. When liquid oxygen is introduced into the gas reforming step, the heat of evaporation thereof and the sensible heat of low-temperature oxygen gas are used as a cooling source for the methanol synthesis step, i.e., a cooling source used in a condenser for separating crude methanol, so that the energy efficiency of the methanol production step can be improved.

In the present invention, the stoichiometric ratio of hydrogen to carbon oxides [$H_2/(2CO + 3CO_2)$] in the feed gas to the methanol synthesis reactor is 1.0 to 2.7, preferably 1.1 to 2.0, more preferably 1.2 to 1.8. When the above stoichiometric ratio is lower than 1.0, the yield of methanol relative to carbon oxides ($CO + CO_2$) [to be referred to as "($CO + CO_2$) yield" hereinafter] is low. When it is higher than 2.7, the volume productivity of methanol is low.

U.S. Patent 4,782,096 describes a process for the production of methanol using a synthesis gas having a stoichiometric ratio of hydrogen to carbon dioxide ($H_2/(2CO + 3CO_2)$) of 1.0 or less, prepared by adding a hydrogen-enriching gas to a synthesis gas.

Conventionally, the optimum stoichiometric ratio of the composition of a gas to be fed to a methanol synthesis reactor is considered to be 1.0. In the present invention, however, it has been found, after detailed studies of the relationship between the productivity and yield of methanol using a fluidized bed catalyst reactor, that the optimum stoichiometric ratio in a practical apparatus is greater than 1.0. Further, the optimum stoichiometric ratio also differs depending upon the CO_2 ratio (CO_2/CO molar ratio) of a feed gas to the reactor. For example, when the CO_2 ratio is 1.2, the optimum stoichiometric ratio is 1.7 to 2.1, and when the CO_2 ratio is 0.6, the optimum stoichiometric ratio is 1.0 to 2.7.

In the present invention, the CO_2 ratio of the feed gas to the methanol synthesis reactor using a fluidized bed catalyst reactor is 0.6 to 1.2, preferably 0.6 to 1.0. When the CO_2 ratio is too low, the temperature in the reactor is liable to increase, and the amount of byproducts such as paraffin may increase. Further, the catalyst may be greatly deactivated. When the CO_2 ratio is too high, the yield of methanol relative to ($CO + CO_2$) decreases, and the amount

of formed H_2O increases. Thus, the catalyst is also liable to be deactivated.

In the self heat-exchanger type reactor for carrying out the primary reforming, partial oxidation and secondary reforming, hydrogen is consumed by partial oxidation as described already, and therefore the stoichiometric ratio of hydrogen to carbon oxides in the feed gas to the methanol synthesis reactor decreases. Further, with an increase in the amount of hydrocarbon having 2 or more carbon atoms contained in the hydrocarbon as a raw material, the stoichiometric ratio further decreases. How to cope with such a decrease in the stoichiometric ratio will be explained below.

In order to cope with a decrease in the stoichiometric ratio first, carbon dioxide gas may be removed from the synthesis gas in Step (a). Carbon dioxide gas can be removed by various methods. For example, the carbon dioxide gas can be removed by allowing crude methanol obtained from the methanol synthesis step to absorb the carbon dioxide gas. The crude methanol may be cooled by the heat of evaporation of liquid oxygen to be used in the gas reforming step and/or by low-temperature oxygen to be used in the gas reforming step before absorbing the carbon dioxide gas.

Further, the heat of evaporation of liquid oxygen to be used in the gas reforming step and the sensible heat of low-temperature oxygen gas to be used in the gas reforming step may be also used as a cooling source for a condenser used for separating crude methanol, and when the temperature for cooling the crude methanol is decreased, the amount of dissolved CO_2 increases. As a result, the stoichiometric ratio in the feed gas to the methanol synthesis reactor increases, and the CO_2 ratio decreases. Therefore, there is obtained a gas composition more preferable for the fluidized bed catalyst reactor.

In order to cope with a decrease in the stoichiometric ratio, there is another method in which carbon dioxide gas is removed from part of the purge gas from the methanol synthesis step in step (b), and that part of the purge gas is fed to the methanol synthesis reactor together with the synthesis gas. In this case, the carbon dioxide can be also removed by the above method. In addition, when carbon dioxide gas is removed as above, the CO_2 ratio in the feed gas to the methanol synthesis reactor is decreased, and it is therefore necessary to control the CO_2 ratio.

In order to cope with a decrease in the stoichiometric ratio, there is further another method in which hydrogen is separated from part of the purge gas in step (d) and the separated hydrogen is fed to the methanol synthesis reactor together with the synthesis gas. In this case, a PSA (pressure swing adsorption) apparatus can be used for recovering hydrogen. Typically, the purge gas from which hydrogen has been separated is used as a fuel for a gas turbine engine. Part of the purge gas or a waste gas from the PSA apparatus can be used as a fuel for a reforming furnace of a conventional steam reforming apparatus, while it can be used as a fuel for a gas turbine engine in the present invention since the process of the present invention requires no reforming furnace.

Further, when the high-pressure steam recovered from the methanol synthesis reactor is heated with waste heat from the gas turbine engine and used as a power source, higher energy efficiency can be obtained.

Figs. 1 to 4 show flow charts of processes for the production of methanol, employing the gas reforming step and the methanol synthesis step used in the present invention.

Fig. 1 shows an embodiment in which methanol is produced by removing a predetermined amount of carbon dioxide gas from the synthesis gas obtained from the gas reforming step with crude methanol and then introducing the remaining synthesis gas into the methanol synthesis reactor.

In Fig. 1, hydrocarbon as a raw material from a flow path 1 and a purge gas (from a methanol synthesis step) from a flow path 16 is mixed, and the mixed gas is passed through a flow path 2. The mixed gas is pressurized with a compressor 30, heated with a heat exchanger 31, and desulfurized with a desulfurizer 32. Then, part of the mixed gas is passed through a flow path 3, heated with a heater 33, then passed through a flow path 4, combined with process steam from a flow path 5, heated with a heat exchanger 34 and then introduced into a gas reforming reactor 7 through a flow path 6.

A primary reforming reaction takes place in an upper portion of the gas reforming reactor 7. Then, a remainder of the mixed gas (hydrocarbon and purge gas), which is passed through a flow path 8, is introduced into a lower portion of the gas reforming reactor 7 together with oxygen from a flow path 9, and a partial oxidation is carried out. Then, a secondary reforming reaction takes place, and then, a reformed gas is recovered through a flow path 10. The secondary reformed gas heats primary reforming reaction tubes.

The reformed gas is used for heat recovery in the heat exchangers 34 and 35, the heater 33 and a heat exchanger 36, and then cooled with a condenser 37 to condense and separate unreacted steam. As a result, a synthesis gas is obtained. A predetermined amount of carbon dioxide gas is removed from the synthesis gas with crude methanol in a carbon dioxide absorption column 10a. Crude methanol cooled using the heat of evaporation of liquid oxygen, etc., is advantageously used as a crude methanol, since the amount of carbon dioxide gas which can be dissolved in the crude methanol increases. The synthesis gas from which carbon dioxide gas has been removed is passed through a flow path 11, pressurized with a compressor 38 which also works as a synthesis gas circulating device, heated with a heat exchanger 39, passed through a flow path 12 and then fed into a fluidized bed catalyst reactor 12a for the synthesis of methanol. The heat of reaction is transmitted to water inside heat-transfer tubes 12b placed inside the reactor 12a, and high-pressure steam is recovered from a separator 41. In Fig. 1, the high-pressure steam is reheated with the heat

exchanger 35 This high-pressure steam can be widely used as the process steam from the flow path 5 and a power source for compressors. Water is fed through a flow path 42, and boiler water is suitable for use

Upstream of the compressor 38 and in the flow path 11 the synthesis gas is combined with a circulating gas branched from a gas from the reactor 12a through a flow path 14. In the reactor 12a a methanol synthesis reaction takes place. A reaction gas from the reactor 12a is subjected to heat recovery with the heat exchanger 39, cooled with a condenser 40, and separated into crude methanol and gas with a high-pressure separator 47. Part of the gas is used as a circulating gas passing through the flow path 14, and another part thereof is passed, as a purge gas. through flow paths 15 and 16 and combined with hydrocarbon as a raw material A remainder of the purge gas is passed through flow paths 17 and 20, and used as a fuel for a gas turbine engine (not shown). The crude methanol is introduced into a low-pressure separator 43 through a flow path 21, and separated into crude methanol and a dissolved gas. Further the dissolved gas is washed with water through a washing column 44 to separate methanol from the dissolved gas. The separated crude methanol for a high-pressure separator 47 is combined with the crude methanol from the low-pressure separator 43 and introduced into a methanol purification apparatus through a flow path 25 The dissolved gas which has been separated is passed through flow paths 22 and 20 and used as a fuel for a gas turbine engine.

Fig. 2 shows a modified embodiment in which methanol is produced by removing a predetermined amount of carbon dioxide gas from part of purge gas from the methanol synthesis step, and then introducing the resultant part of purge gas into a reactor 12a together with a synthesis gas.

In Fig. 2, a purge gas is passed through flow paths 15 and 17, and then in a carbon dioxide absorption column 17a, crude methanol absorbs carbon dioxide gas to remove it from the purge gas. Crude methanol cooled to a low temperature is advantageous as such, since the amount of dissolved carbon dioxide gas increases. The purge gas from which carbon dioxide gas has been removed is pressurized with a compressor 45. passed through a flow path 19, combined with a synthesis gas from a flow path 11 downstream of a compressor 38, and introduced into a reactor 12a

Fig. 3 shows a modified embodiment in which a gas from a fluid catalyst reactor 12a is cooled by the heat of evaporation of liquid oxygen to be used in the gas reforming step and the sensible heat of low-temperature oxygen to be used in the gas reforming step, and a separated gas portion is fed to the reactor 12a as a circulating gas together with the synthesis gas.

The reaction gas from the fluid catalyst reactor 12a is subjected to heat recovery with a heat exchanger 39, cooled with a condenser 40 and cooled with a crude methanol condenser 26 to be separated into crude methanol and gas The crude methanol condenser 26 uses the heat of evaporation of liquid oxygen and the sensible heat of low-temperature oxygen gas for cooling the reaction gas, so that the crude methanol can be cooled to a very low temperature, and the amount of carbon dioxide gas which can be dissolved in methanol can be remarkably increased.

Fig. 4 shows a modified embodiment in which hydrogen is separated from part of a purge gas obtained from the methanol synthesis step with a pressure swing method adsorption (PSA) apparatus, and the separated hydrogen is introduced into a reactor 12a to produce methanol.

A purge gas from a flow path 17 is introduced into a PSA apparatus 27 to separate hydrogen. and the separated hydrogen is pressurized with a compressor 46. passed through a flow path 28, combined with a synthesis gas upstream of a compressor 38 and introduced into the reactor 12a The purge gas from which hydrogen has been separated is passed through flow paths 18 and 20, and used as a fuel for a gas turbine engine.

The present invention will be explained more in detail hereinafter with reference to Examples However, the present invention shall not be limited to these Examples.

Comparative Examples 1 - 2

Methanol was synthesized by means of a methanol synthesis test apparatus having a fluidized bed catalyst reactor having an internal diameter of 0.31 m and a height of 20 m. A Cu-Zn-Zr-Al catalyst (average particle diameter 60 μm particle density 2.39 g/cm^3) was used as a fluid catalyst. The reactor inlet gas temperature and pressure were set at 200°C 80 0 kg/cm^2G, SV = 9,310 (l/h), LV = 0 51 m/sec. the boiler water temperature was set at 230°C. and the circulation ratio (circulating gas/synthesis gas) was set at 3.0 Under these conditions. mixed gases having various compositions were respectively reacted. Table 1 shows the results.

Table 1

	CEx 1	CEx 2
Composition of synthesis gas (vol%)		
CO	20.00	10 79
CO_2	10.85	10 79

Table 1 (continued)

	CEx 1	CEx 2
Composition of synthesis gas (vol%)		
H_2	66.22	75.50
CH_4	2.39	2.39
N_2	0.45	0.45
H_2O	0.09	0.09
Composition of gas in reactor inlet (vol%)		
CO	9.38	4.07
CO_2	16.94	5.32
H_2	49.99	82.70
CH_4	19.32	6.25
N_2	3.91	1.19
H_2O	0.04	0.05
CH_3OH	0.42	0.42
Stoichiometric ratio	0.72	3.43
CO_2 ratio	1.81	1.31
Yield based on CO + CO_2 (%)	87.5	90.3
Methanol production (ton/day)	10.3	7.4

Example 1

According to the flow shown in Fig. 1, carbon dioxide gas was removed from a gas prepared with a gas reforming apparatus, and the resultant gas was introduced into a synthesis apparatus to produce methanol.

The main reaction conditions in the gas reforming apparatus and the methanol synthesis apparatus were as follows.

Primary reforming inlet temperature	500°C
Primary reforming inlet pressure	83.0 kg/cm²G
Primary reforming outlet temperature	790°C
Secondary reforming outlet temperature	1,030°C
Reforming reactor outlet temperature	551°C
Reforming reactor outlet pressure	79.7 kg/cm²G
Methanol synthesis reactor inlet temperature	198°C
Methanol synthesis reactor outlet temperature	263°C
Methanol synthesis reactor pressure	80.0 kg/cm²G
Stoichiometric ratio in methanol synthesis reactor inlet	1.67
CO_2 ratio in methanol synthesis reactor inlet	0.997
Yield based on CO + CO_2	93.3 %

Tables 2 to 6 show flow amounts and compositions in main portions in the case of the production of 5.000 tons/day of methanol. In Tables 2 to 6, values for CH_3OH include values of byproduct. As a result, there was obtained a methanol process achieving an energy unit consumption of 6.948 MMkcal per ton of purified methanol.

Table 2

Hydrocarbons as raw material	Flow division (1) (flow path 3) (kg-mol/h)	Flow division (2) (flow path 8) (kg-mol/h)	Composition (mol%)
CH_4	3,250.4	2,167.1	78.68
C_2H_6	270.8	180.5	6.55
C_3H_8	105.2	70.2	2.55
C_4H_{10}	48.2	32.1	1.17
C_5H_{12}	16.4	10.9	0.40

Table 2   (continued)

Hydrocarbons as raw material	Flow division (1) (flow path 3) (kg-mol/h)	Flow division (2) (flow path 8) (kg-mol/h)	Composition (mol%)
C_6H_{14}	5 5	3.8	0 14
CO	19 7	13.2	0 48
CO_2	56 0	37.3	1 36
H_2	330.5	220.4	8 00
N_2	24 8	16 5	0 60
H_2O	0 2	0.1	0 00
CH_3OH	3.0	2.0	0.07
Total	4,130 7	2,754 1	100 00

Table 3

	Steam as raw material (flow path 5) 12,846.8 kg-mol/h	Oxygen gas (flow path 9)	
O_2	3,015.2 kg-mol/h	99.50 mol%
N_2	15.2	0.50
Total	3,030.4	100 00

Table 4

	Secondary reforming outlet gas (flow path 10)		Synthesis gas (flow path 11)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	555.9	1 53	511.9	2.21
CO_2	2,132.8	5 86	1,994.3	8 62
CO	4,806.4	13 20	4,780.7	20.67
H_2	15,783.6	43 33	15,751.8	68.11
N_2	56.5	0 16	56.0	0 24
H_2O	13,086 3	35 92	4.9	0 02
CH_3OH			30 4	0 13
Total	36,421.5	100.00	23,130.0	100.00

Table 5

	Synthesis reactor inlet gas (flow path 12)		Outlet gas (flow path 13)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	22,426.1	21 42	22,426.1	24.45
CO_2	7,618.9	7 28	5 841.1	6.37
CO	7,638.1	7 29	2 922.2	3 19
H_2	63,600.0	60 73	48,835.0	53 22
N_2	2,923.7	2 79	2,923.7	3.19
H_2O	36.7	0 04	1 820.9	1.99
CH_3OH	468.3	0.45	6 955.5	7.59
Total	104,711.8	100.00	91 724.5	100.00

Table 6

	Circulating gas (flow path 14)		Crude methanol (flow path 25)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	21,917.7	26.87	0.9	0.01
CO_2	5,624.5	6.89	18.9	0.22
CO	2,857.4	3.50	0.1	0.00
H_2	47,850.3	58.65	0.0	0.00
N_2	2,864.1	3.51	0.0	0.00
H_2O	31.8	0.04	2,198.4	25.19
CH_3OH	438.0	0.54	6,507.3	74.57
Total	81,583.8	100.00	8,725.6	100.00

Amount of purge gas	
(flow path 15)	1,615.04 kg-mol/h
(flow path 16)	939.27 kg-mol/h

Example 2

According to the flow shown in Fig. 2, carbon dioxide gas was removed from part of a purge gas from a methanol synthesis apparatus with crude methanol, and the resultant gas was introduced into a synthesis apparatus to produce methanol.

The main reaction conditions in the gas reforming apparatus and the methanol synthesis apparatus were as follows.

Primary reforming inlet temperature	500°C
Primary reforming inlet pressure	83.0 kg/cm²G
Primary reforming outlet temperature	790°C
Secondary reforming outlet temperature	1,030°C
Reforming reactor outlet temperature	564°C
Reforming reactor outlet pressure	79.7 kg/cm²G
Methanol synthesis reactor inlet temperature	198°C
Methanol synthesis reactor outlet temperature	263°C
Methanol synthesis reactor pressure	80.0 kg/cm²G
Stoichiometric ratio in methanol synthesis reactor inlet	1.27
CO_2 ratio in methanol synthesis reactor inlet	1.08
Yield based on $CO + CO_2$	94.5 %

Tables 7 to 11 show flow amounts and compositions in main portions in the case of the production of 5,000 ton/day of methanol. In Tables 7 to 11, values for CH_3OH include values of byproduct. As a result, there was obtained a methanol process achieving an energy unit consumption of 6.930 MMkcal per ton of purified methanol.

Table 7

Gas reforming apparatus	Flow division (1) (flow path 3) (kg-mol/h)	Flow division (2) (flow path 8) (kg-mol/h)	Composition (mol%)
CH_4	3,306.2	2,208.0	79.43
C_2H_6	267.2	178.4	6.42
C_3H_8	103.9	69.3	2.50
C_4H_{10}	47.6	31.7	1.14
C_5H_{12}	16.2	10.8	0.39
C_6H_{14}	5.6	3.8	0.14

Table 7   (continued)

Gas reforming apparatus	Flow division (1) (flow path 3) (kg-mol/h)	Flow division (2) (flow path 8) (kg-mol/h)	Composition (mol%)
CO	28.2	18.8	0.68
CO_2	67.6	45.2	1.62
H_2	289.6	193.4	6.96
N_2	25.8	17.3	0.62
H_2O	0.2	0.2	0.01
CH_3OH	3.6	2.4	0.09
Total	4,161.7	2,779.3	100.00

Table 8

	Steam as raw material (flow path 5) 10,520.3 kg-mol/h	Oxygen gas (flow path 9)
O_2	3,013.5 kg-mol/h	99.50 mol%
N_2	15.1	0.50
Total	3,028.6	100

Table 9

	Secondary reforming outlet gas (flow path 10)		Synthesis gas (flow path 11)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	721.5	2.13	721.5	3.15
CO_2	1,907.7	5.64	1,907.7	8.32
CO	4,980.6	14.73	4,980.6	21.72
H_2	15,235.2	45.06	15,235.2	66.45
N_2	58.2	0.17	58.2	0.25
H_2O	10,907.7	32.26	26.0	0.11
Total	33,810.9	100.00	22,929.2	100.00

Table 10

	Synthesis reactor inlet gas (flow path 12)		Outlet gas (flow path 13)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	43,214.6	32.53	43,214.6	36.08
CO_2	10,546.8	7.94	8,922.5	7.45
CO	9,803.4	7.38	4,894.2	4.09
H_2	64,955.6	48.89	50,263.7	41.96
N_2	3,635.2	2.74	3,635.2	3.03
H_2O	69.4	0.05	1,706.7	1.42
CH_3OH	626.5	0.48	7,146.9	5.97
Total	132,851.5	100.00	119,783.8	100.00

Table 11

	Circulating gas (flow path 14)		Crude methanol (flow path 25)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	42,273.5	38.72	7.1	0.08

Table 11 (continued)

	Circulating gas (flow path 14)		Crude methanol (flow path 25)	
	kg-mol/h	mol%	kg-mol/h	mol%
CO_2	8,628.8	7 90	35.7	0.41
CO	4,789.4	4 39	0 6	0.01
H_2	49,268.0	45 13	0.4	0.00
N_2	3,562 5	3 26	0 0	0 00
H_2O	40.1	0 04	2,077 5	24 07
CH_3OH	612 9	0 56	6 509 7	75 43
Total	109,175.2	100 00	8,631 0	100 00

Amount of purge gas	
(flow path 15)	2,140 80 kg-mol/h
(flow path 16)	1,070 40 kg-mol/h

Example 3

According to the flow shown in Fig. 3, the heat of evaporation of liquid oxygen used in the gas reforming step and the sensible heat of low-temperature oxygen were used as a cooling source in the methanol synthesis apparatus to produce methanol.

In Fig. 3, a crude methanol condensor 26 using the heat of evaporation of liquid oxygen and the sensible heat of low-temperature oxygen was placed before a crude methanol high-pressure separator.

The main reaction conditions in the gas reforming apparatus and the methanol synthesis apparatus were as follows

Primary reforming inlet temperature	500°C
Primary reforming inlet pressure	83.0 kg/cm²G
Primary reforming outlet temperature	790°C
Secondary reforming outlet temperature	1,030°C
Reforming reactor outlet temperature	564°C
Reforming reactor outlet pressure	79.7 kg/cm²G
Methanol synthesis reactor inlet temperature	198°C
Methanol synthesis reactor outlet temperature	263°C
Methanol synthesis reactor pressure	80.0 kg/cm²G
Stoichiometric ratio in methanol synthesis reactor inlet	1.39
CO_2 ratio	1 12
Yield based on $CO + CO_2$	94.0 %

Tables 12 to 16 show flow amounts and compositions in main portions in the case of the production of 5.000 ton/day of methanol. In Tables 12 to 16, values for CH_3OH include values of byproduct. As a result, there was obtained a methanol process achieving an energy consumption unit of 6 917 MMkcal per ton of purified methanol.

In addition, when the heat of evaporation of liquid oxygen and the sensible heat of low-temperature oxygen gas were not used in the above process the stoichiometric ratio in methanol synthesis reactor inlet was 1 07 the CO_2 ratio was 1.31, the yield based on $CO + CO_2$ was 94.0 %, and the energy consumption unit per ton of purified methanol was 6.929 MMkcal.

Table 12

Gas reforming apparatus	Flow division (1) (flow path 3) (kg-mol/h)	Flow division (2) (flow path 8) (kg-mol/h)	Composition (mol%)
CH_4	3,242.7	2.162.2	78 37
C_2H_6	267.6	178.4	6 47
C_3H_8	104.1	69.4	2 51

Table 12 (continued)

Gas reforming apparatus	Flow division (1) (flow path 3) (kg-mol/h)	Flow division (2) (flow path 8) (kg-mol/h)	Composition (mol%)
C_4H_{10}	47.6	31.7	1.15
C_5H_{12}	16.2	10.8	0.39
C_6H_{14}	5.6	3.8	0.14
CO	24.1	16.1	0.58
CO_2	68.3	45.5	1.65
H_2	331.3	220.9	8.00
N_2	29.6	19.7	0.72
H_2O	0.1	0.0	0.00
CH_3OH	1.0	0.6	0.02
Total	4,138.2	2,759.1	100.00

Table 13

Steam as raw material (flow path 5) 12,776.6 kg-mol/h Oxygen gas (flow path 9)		
O_2	3,003.2 kg-mol/h	99.50 mol%
N_2	15.1	0.50
Total	3,018.3	100.00

Table 14

	Secondary reforming outlet gas (flow path 10)		Synthesis gas (flow path 11)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	553.6	1.53	553.2	2.38
CO_2	2,133.5	5.88	2,121.5	9.13
CO	4,797.2	13.22	4,794.0	20.62
H_2	15,697.2	43.26	15,685.7	67.48
N_2	64.4	0.18	64.4	0.28
H_2O	13,038.4	35.93	26.4	0.11
Total	36,284.3	100.00	23,245.2	100.00

Table 15

	Synthesis reactor inlet gas (flow path 12)		Outlet gas (flow path 13)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	24,449.0	23.37	24,449.0	26.70
CO_2	8,949.3	8.56	7,154.4	7.81
CO	7,997.9	7.65	3,275.4	3.58
H_2	59,700.5	57.07	44,870.7	48.99
N_2	3,341.7	3.19	3,341.7	3.65
H_2O	33.9	0.03	1,835.3	2.00
CH_3OH	130.2	0.13	6,654.1	7.27
Total	104,602.5	100.00	91,580.6	100.00

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Table 16

	Circulating gas (flow path 14)		Crude methanol (flow path 25)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	23,896.1	29.37	1.1	0.01
CO_2	6,827.9	8.39	41.7	0.47
CO	3,203.8	3.94	0.1	0.00
H_2	44,015.4	54.10	0.0	0.00
N_2	3,276.9	4.03	0.0	0.00
H_2O	7.5	0.01	2,237.8	25.46
CH_3OH	130.2	0.16	6,507.7	74.06
Total	81,357.8	100.00	8,788.4	100.00

Amount of purge gas	
(flow path 15)	1,521.28 kg-mol/h
(flow path 16)	500.74 kg-mol/h

Example 4

According to the flow shown in Fig. 4, hydrogen separated from a purge gas from a methanol synthesis apparatus with a PSA (pressure swing method adsorption) apparatus was introduced into the methanol synthesis apparatus to produce methanol.

In Fig. 4, hydrogen was separated from a purge gas from the flow path 17 with the PSA apparatus 27, and introduced into the methanol synthesis apparatus through the flow path 28 together with reformed gas.

The main reaction conditions in the gas reforming apparatus and the methanol synthesis apparatus were as follows.

Primary reforming inlet temperature	500°C
Primary reforming inlet pressure	83.0 kg/cm²G
Primary reforming outlet temperature	790°C
Secondary reforming outlet temperature	1,031°C
Reforming reactor outlet temperature	569°C
Reforming reactor outlet pressure	79.7 kg/cm²G
Methanol synthesis reactor inlet temperature	198°C
Methanol synthesis reactor outlet temperature	263°C
Methanol synthesis reactor pressure	80.0 kg/cm²G
Stoichiometric ratio in methanol synthesis reactor inlet	1.45
CO_2 ratio	0.995
Yield based on $CO + CO_2$	93.9 %

Tables 17 to 21 show flow amounts and compositions in main portions in the case of the production of 5.000 ton/day of methanol. As a result, there was obtained a methanol process achieving an energy consumption unit of 6.846 MMkcal per ton of purified methanol.

Table 17

Gas reforming apparatus	Flow division (1) (flow path 3) (kg-mol/h)	Flow division (2) (flow path 8) (kg-mol/h)	Composition (mol%)
CH_4	3,380.6	2.253.5	78.67
C_2H_6	277.4	184.9	6.45
C_3H_8	107.8	71.9	2.51
C_4H_{10}	49.3	32.9	1.15
C_5H_{12}	16.8	11.2	0.39

Table 17   (continued)

Gas reforming apparatus	Flow division (1) (flow path 3) (kg-mol/h)	Flow division (2) (flow path 8) (kg-mol/h)	Composition (mol%)
C_6H_{14}	5.9	3.9	0.14
CO	26.9	18.0	0.63
CO_2	66.6	44.5	1.55
H_2	343.6	229.0	8.00
N_2	18.4	12.2	0.43
H_2O	0.1	0.1	0.00
CH_3OH	3.6	2.4	0.08
Total	4,297.0	2,864.5	100.00

Table 18

Steam as raw material (flow path 5) 10,809.6 kg-mol/h		Oxygen gas (flow path 9)
O_2	3,068.4 kg-mol/h	99.50 mol%
N_2	15.4	0.50
Total	3,083.8	100.00

Table 19

	Secondary reforming outlet gas (flow path 10)		Synthesis gas (flow path 11)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	767.3	2.22	767.3	3.21
CO_2	1,943.7	5.61	1,943.7	8.13
CO	5,070.2	14.65	5,070.2	21.20
H_2	15,613.2	45.11	16,071.3	67.18
N_2	46.0	0.13	46.0	0.19
H_2O	11,172.3	32.28	21.8	0.09
Total	34,612.7	100.00	23,920.3	100.00

Table 20

	Synthesis reactor inlet gas (flow path 12)		Outlet gas (flow path 13)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	29,325.1	25.93	29,325.1	29.37
CO_2	8,760.3	7.74	7,115.3	7.12
CO	8,806.3	7.79	3,831.0	3.84
H_2	63,774.6	56.39	48,869.1	48.96
N_2	1,888.0	1.67	1,888.0	1.89
H_2O	41.7	0.04	1,699.9	1.70
CH_3OH	497.5	0.44	7,103.9	7.12
Total	113,093.5	100.00	99,852.5	100.00

Table 21

	Circulating gas (flow path 14)		Crude methanol (flow path 25)	
	kg-mol/h	mol%	kg-mol/h	mol%
CH_4	28,557.8	32.03	5.6	0.06
CO_2	6,816.6	7.64	47.4	0.54
CO	3,736.1	4.19	0.2	0.00
H_2	47,703.3	53.49	0.9	0.01
N_2	1,842.0	2.07	0.0	0.00
H_2O	19.9	0.02	2,095.7	23.97
CH_3OH	497.0	0.56	6.595.1	75.42
Total	89,172.7	100.00	8,744.9	100.00

Amount of purge gas	
(flow path 15)	2,140.8 kg-mol/h
(flow path 16)	1,070.4 kg-mol/h

The fluidized bed catalyst reactor has the following advantages. (1) Not only gas but also catalyst particles come into contact with heat-transfer tubes in the reactor so that a high efficiency of heat transfer can be achieved. (2) The heat is well diffused in the catalyst layer so that the reaction temperature is uniform, and there is no local rise in temperature. As a result, the reactivity can be improved, and the concentration of active components ($CO + CO_2$) can be increased. The amount of a circulating gas can be therefore decreased. (3) Due to a uniform temperature distribution and high efficiency of heat transfer, the high-pressure steam recovered has an elevated pressure. (4) The pressure loss in the reactor is remarkably small as compared with a multi-tube reactor having a fixed catalyst bed. (5) The reaction temperature is uniform and there is no local rise in temperature so that the amount of byproducts is small, and the heat efficiency in the distillation and purification steps can be improved.

The process of the present invention uses a combination of a gas reforming step in which a primary reformed gas is partially oxidized and secondary reformed and the resultant high-temperature secondary reformed gas is used as a heat source for the primary reforming, and a fluidized bed catalyst reactor having the above-described advantages and the present invention defines the composition of a feed gas to the reactor. When the reaction conditions and process are selected such that they are suited for the defined composition of a feed gas. there can be provided a process for the production of methanol, which process permits an increase in the capacity of an apparatus for the production of methanol with high energy efficiency.

Claims

1. A process for the production of methanol, comprising a primary reforming step of catalytically reacting a hydrocarbon as a raw material with steam, a partial oxidation step of partially oxidizing a gas fed from the above primary reforming step by adding an oxygen gas, a secondary reforming step of catalytically reacting a gas fed from the above partial oxidation step with steam, a step of using a high-temperature gas obtained from the secondary reforming step as a heat source for the primary reforming step, a synthesis gas preparation step of separating steam from the gas used as the above heat source to prepare a synthesis gas, and a methanol synthesis step which comprises introducing the synthesis gas into a methanol synthesis reactor with a fluid bed catalyst,
   wherein:

   - a proportion of a gas from the methanol synthesis reactor is re-introduced into the methanol synthesis reactor as a circulating gas together with the synthesis gas.
   - a remaining part of the gas from the methanol synthesis reactor is introduced into the primary reforming step as a purge gas together with the hydrocarbon as a raw material; and
   - at least one step selected from (a), (b), (c) and (d) is carried out to bring the molar ratio of hydrogen to carbon oxides in a feed gas to be introduced into the methanol synthesis reactor, represented by $[H_2/(2CO + 3CO_2)]$ to from 1.0 to 2.7 and to bring the molar ratio of CO_2/CO in the feed gas to from 0.6 to 1.2.

(a) introducing the synthesis gas into the methanol synthesis reactor after carbon dioxide gas is removed from the synthesis gas;

(b) removing carbon dioxide gas from part of the purge gas, and introducing that part of the purge gas into the methanol synthesis reactor together with the synthesis gas

(c) cooling the gas obtained from the methanol synthesis step with the heat of evaporation of liquid oxygen to be used in the gas reforming step and/or by low temperature oxygen to be used in the gas reforming step, to divide the gas into a feed gas and crude methanol which can dissolve a large amount of carbon dioxide gas, and feeding the feed gas as a circulating gas, to the methanol synthesis reactor together with the synthesis gas; and

(d) separating hydrogen from part of the purge gas and feeding the separated hydrogen to the methanol synthesis reactor together with the synthesis gas.

2. A process according to claim 1 wherein the process comprises

    a a primary reforming step of mixing part of the purge gas with the hydrocarbon as a raw material to prepare a mixed gas, adjusting 40 to 80 mol% of the mixed gas to have a molar ratio (S/C) of steam (S) to hydrocarbon (C) of 1.5 to 4.0 and introducing the adjusted mixed gas into the primary reforming step to carry out the primary reforming reaction such that outlets of reaction tubes show a pressure of 25 to 95 atmospheric pressure and a temperature of 700 to 800°C.

    b. a partial oxidation step of adding oxygen gas in an amount of 0.40 to 0.46 mol per mole of total carbon of hydrocarbon as a raw material to a primary reformed gas and a remainder of the above mixed gas to carry out a partial oxidation, and

    c a step of using a secondary reformed gas obtained from the secondary reforming step as a heat source for the primary reforming step, separating unreacted steam by heat recovery and cooling, and introducing the synthesis gas into the methanol synthesis reactor

3. A process according to claim 1 or 2, wherein the synthesis gas is introduced into the methanol synthesis reactor through a compression step.

4. A process according to any one of the preceding claims, wherein the carbon dioxide gas is removed from the synthesis gas in step (a), by allowing crude methanol obtained from the methanol synthesis step to absorb the carbon dioxide gas.

5. A process according to claim 4, wherein the crude methanol is cooled by the heat of evaporation of liquid oxygen to be used in the gas reforming step and/or by low-temperature oxygen to be used in the gas reforming step before absorbing the carbon dioxide gas.

6. A process according to any one of the preceding claims wherein the hydrogen is separated from part of the purge gas in step (d), with a pressure swing adsorption apparatus

7. A process according to claim 6, wherein the purge gas from which hydrogen has been separated is used as a fuel for a gas turbine engine.

8. A process according to any one of the preceding claims wherein part of the purge gas is used as a fuel for a gas turbine engine

Patentansprüche

1. Verfahren zur Herstellung von Methanol, umfassend eine erste Reformierstufe der katalytischen Umsetzung eines Kohlenwasserstoffes als Rohmaterial mit Dampf, eine partielle Oxidationsstufe der partiellen Oxidierung eines Ausgangsgases aus der obigen ersten Reformierstufe durch Zusatz von Sauerstoffgas, eine zweite Reformierstufe der katalytischen Umsetzung eines Ausgangsgases aus der obigen partiellen Oxidationsstufe mit Dampf, eine Stufe der Anwendung eines Gases mit hoher Temperatur erhalten aus der zweiten Reformierstufe, als Wärmequelle für die erste Reformierstufe, eine Stufe der Synthesegasherstellung durch Abtrennung von Dampf aus dem als die oben angegebene Wärmequelle verwendeten Gas zur Herstellung eines Synthesegases, und eine Stufe der Methanolsynthese umfassend das Einführen des Synthesegases in einen Methanolsynthesereaktor mit einem Fluidbettkatalysator, wobei

- ein Anteil eines Gases aus dem Methanolsynthesereaktor erneut in den Methanolsynthesereaktor als umlaufendes Gas zusammen mit dem Synthesegas eingeleitet wird,

- ein restlicher Teil des Gases aus dem Methanolsynthesereaktor in die erste Reformierstufe als Spülgas zusammen mit dem Kohlenwasserstoff als Rohmaterial eingeleitet wird, und

- mindestens eine Stufe, ausgewählt aus (a), (b), (c) und (d), durchgeführt wird, um das Molverhältnis von Wasserstoff zu Kohlenoxiden in einem Speisegas, das in den Methanolsynthesereaktor eingeleitet wird, angegeben durch [$H_2/(2CO + 3CO_2)$] auf 1,0 bis 2,7 zu bringen und das Molverhältnis CO_2/CO in dem Speisegas auf 0,6 bis 1,2 zu bringen,

(a) Einleiten des Synthesegases in den Methanolsynthesereaktor, nachdem Kohlendioxidgas von dem Synthesegas entfernt worden ist;

(b) Entfernen von Kohlendioxidgas von einem Teil des Spülgases und Einleiten jenes Teils des Spülgases in den Methanolsynthesereaktor zusammen mit dem Synthesegas;

(c) Kühlen des in der Methanolsynthesestufe erhaltenen Gases mittels der Verdampfungswärme von flüssigem Sauerstoff, der in der Gasreformierstufe verwendet werden soll, und/oder durch Sauerstoff niedriger Temperatur, der in der Gasreformierstufe verwendet werden soll, um das Gas in ein Speisegas und rohes Methanol zu trennen, das eine große Menge Kohlendioxidgas lösen kann, und Einleiten des Speisegases als umlaufendes Gas in den Methanolsynthesereaktor zusammen mit dem Synthesegas, und

(d) Abtrennen von Wasserstoff von einem Teil des Spülgases und Einleiten des abgetrennten Wasserstoffs in den Methanolsynthesereaktor zusammen mit dem Synthesegas

2. Verfahren nach Anspruch 1, wobei das Verfahren umfaßt:

a) eine erste Reformierstufe des Mischens eines Teils des Spülgases mit dem Kohlenwasserstoff als Rohmaterial zur Erzeugung eines gemischten Gases, Einstellen von 40 bis 80 Mol-% des gemischten Gases auf ein Molverhältnis (D/K), von Dampf (D) zu Kohlenwasserstoff (K) von 1,5 bis 4,0 und Einleiten des eingestellten gemischten Gases in die erste Reformierstufe zur Durchführung der ersten Reformierreaktion, so daß an den Auslaßöffnungen der Reaktionsrohre ein Druck von 25 bis 95 Atmosphären und eine Temperatur von 700 bis 800°C herrscht.

b) eine partielle Oxidationsstufe der Zugabe von Sauerstoffgas in einer Menge von 0,40 bis 0,46 Mol pro Mol Gesamtkohlenstoff des Kohlenwasserstoffs als Ausgangsmaterial zu einem ersten reformierten Gas und einem Rest des oben angegebenen gemischten Gases zur Durchführung einer partiellen Oxidation, und

c) eine Stufe der Verwendung eines zweiten reformierten Gases, das aus der zweiten Reformierstufe erhalten worden ist, als Wärmequelle für die erste Reformierstufe, des Abtrennens von nicht umgesetztem Dampf durch Wärmerückgewinnung und Kühlen und des Einleitens des Synthesegases in den Methanolsynthesereaktor.

3. Verfahren nach Anspruch 1 oder 2, wobei das Synthesegas in den Methanolsynthesereaktor über eine Kompressionsstufe eingeleitet wird.

4. Verfahren nach einem der vorangehenden Ansprüche, wobei das Kohlendioxidgas von dem Synthesegas in Stufe (a) entfernt wird, indem man rohes Methanol, das aus der Methanolsynthesestufe erhalten worden ist, das Kohlendioxidgas absorbieren läßt.

5. Verfahren nach Anspruch 4, wobei das rohe Methanol gekühlt wird mittels der Verdampfungswärme von flüssigem Sauerstoff, der in der Gasreformierstufe verwendet werden soll, und/oder durch Sauerstoff niedriger Temperatur, der in der Gasreformierstufe verwendet werden soll, vor dem Absorbieren des Kohlendioxidgases.

6. Verfahren nach einem der vorangehenden Ansprüche, wobei der Wasserstoff von einem Teil des Spülgases in Stufe (d) abgetrennt wird mit Hilfe einer Druckschwankungsadsorptionsvorrichtung.

7. Verfahren nach Anspruch 6, wobei das Spülgas, von dem Wasserstoff abgetrennt worden ist, als Treibstoff für einen Gasturbinenmotor verwendet wird

8. Verfahren nach einem der vorangehenden Ansprüche, wobei ein Teil des Spülgases als Treibstoff für einen Gasturbinenmotor verwendet wird

Revendications

1. Procédé pour produire du méthanol, qui comprend une étape de réformage primaire consistant à effectuer une réaction catalytique entre un hydrocarbure, comme matière première, et de la vapeur d'eau, une étape d'oxydation partielle consistant à oxyder partiellement le gaz provenant de l'étape de réformage primaire précédente en ajoutant de l'oxygène gazeux, une étape de réformage secondaire consistant à effectuer une réaction catalytique entre le gaz provenant de l'étape d'oxydation partielle précédente, et de la vapeur d'eau, une étape consistant à utiliser un gaz à haute température provenant de l'étape de réformage secondaire comme source de chaleur pour l'étape de réformage primaire, une étape de préparation d'un gaz de synthèse consistant à séparer la vapeur d'eau du gaz utilisé comme source de chaleur ci-dessus pour préparer un gaz de synthèse, et une étape de synthèse du méthanol qui comprend l'introduction du gaz de synthèse dans un réacteur de synthèse du méthanol avec un catalyseur à lit fluide,
dans lequel

- on ré-introduit une proportion du gaz provenant du réacteur de synthèse du méthanol, dans le réacteur de synthèse du méthanol comme gaz circulant, avec le gaz de synthèse ;
- on introduit la partie restante du gaz provenant du réacteur de synthèse du méthanol dans l'étape de réformage primaire comme gaz de purge, avec l'hydrocarbure comme matière première ; et
- on effectue au moins une étape choisie parmi (a), (b). (c) et (d) pour amener le rapport molaire de l'hydrogène aux oxydes de carbone, dans le gaz d'alimentation qu'il faut introduire dans le réacteur de synthèse du méthanol, représenté par $[H_2/(2CO + 3CO_2)]$, à une valeur de 1,0 à 2,7, et pour amener le rapport molaire CO_2/CO dans le gaz d'alimentation à une valeur de 0,6 à 1 2 :

(a) introduction du gaz de synthèse dans le réacteur de synthèse du méthanol après que le dioxyde de carbone gazeux ait été éliminé du gaz de synthèse ;
(b) élimination du dioxyde de carbone gazeux d'une partie du gaz de purge, et introduction de cette partie du gaz de purge dans le réacteur de synthèse du méthanol avec le gaz de synthèse ;
(c) refroidissement du gaz provenant de l'étape de synthèse du méthanol au moyen de la chaleur d'évaporation de l'oxygène liquide qu'il faut utiliser dans l'étape de réformage du gaz. et/ou au moyen de l'oxygène à basse température qu'il faut utiliser dans l'étape de réformage du gaz, pour diviser le gaz en un gaz d'alimentation et en méthanol brut qui peut dissoudre une grande quantité de dioxyde de carbone gazeux, et alimentation du réacteur de synthèse du méthanol. en gaz d'alimentation, en tant que gaz circulant, avec le gaz de synthèse ; et
(d) séparation entre l'hydrogène et la partie du gaz de purge, et alimentation du réacteur de synthèse du méthanol en hydrogène séparé avec le gaz de synthèse.

2. Procédé conforme à la revendication 1. dans lequel le procédé comprend :

a. une étape de réformage primaire consistant à mélanger une partie du gaz de purge avec l'hydrocarbure comme matière première. pour préparer un gaz mixte. à ajuster 40 à 80 % en moles du gaz mixte pour avoir un rapport molaire (V/HC) de vapeur d'eau (V) à l'hydrocarbure (HC) de 1,5 à 4 0, et à introduire le gaz mixte ajusté dans l'étape de réformage primaire pour effectuer la réaction de réformage primaire de telle façon que les sorties des tubes réactionnels présentent une pression de 25 à 95 pressions atmosphériques et une température de 700 à 800° C,
b. une étape d'oxydation partielle consistant à ajouter de l'oxygène gazeux en une quantité de 0,40 à 0,46 mole par mole de carbone total de l'hydrocarbure comme matière première. à un gaz réformé primaire et un reste du gaz mixte précédent pour effectuer une oxydation partielle, et
c une étape consistant à utiliser un gaz réformé secondaire provenant de l'étape de réformage secondaire comme source de chaleur pour l'étape de réformage primaire, à séparer la vapeur d'eau n'ayant pas réagi par récupération de chaleur et refroidissement, et à introduire le gaz de synthèse dans le système de synthèse du méthanol

3. Procédé conforme à la revendication 1 ou 2. dans lequel on introduit le gaz de synthèse dans le réacteur de synthèse du méthanol par l'intermédiaire d'une étape de compression.

4. Procédé conforme à l'une quelconque des précédentes revendications, dans lequel le dioxyde de carbone gazeux est éliminé du gaz de synthèse dans l'étape (a), en laissant le méthanol brut provenant de l'étape de synthèse du méthanol, absorber le dioxyde de carbone gazeux

5. Procédé conforme à la revendication 4, dans lequel on refroidit le méthanol brut au moyen de la chaleur d'évaporation de l'oxygène liquide qu'il faut utiliser dans l'étape de réformage du gaz, et/ou au moyen de l'oxygène à basse température qu'il faut utiliser dans l'étape de réformage de gaz avant l'absorption du dioxyde de carbone gazeux

6. Procédé conforme à l'une quelconque des précédentes revendications, dans lequel l'hydrogène est séparé de la partie du gaz de purge dans l'étape (d), avec un appareil d'adsorption avec régénération par variation de pression

7. Procédé conforme à la revendication 6, dans lequel le gaz de purge à partir duquel l'hydrogène a été séparé, est utilisé comme carburant pour un moteur à turbine à gaz.

8. Procédé conforme à l'une quelconque des précédentes revendications, dans lequel une partie du gaz de purge est utilisé comme carburant pour un moteur à turbine à gaz.
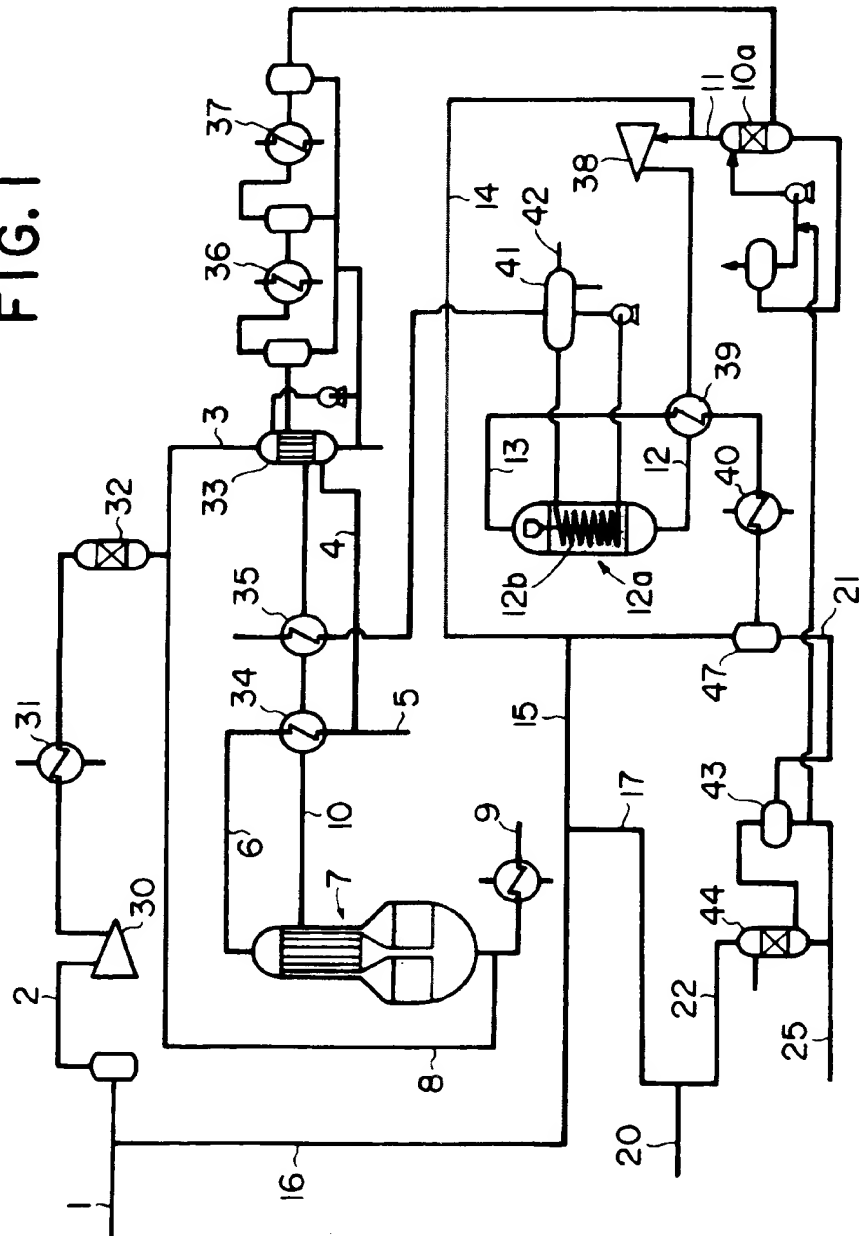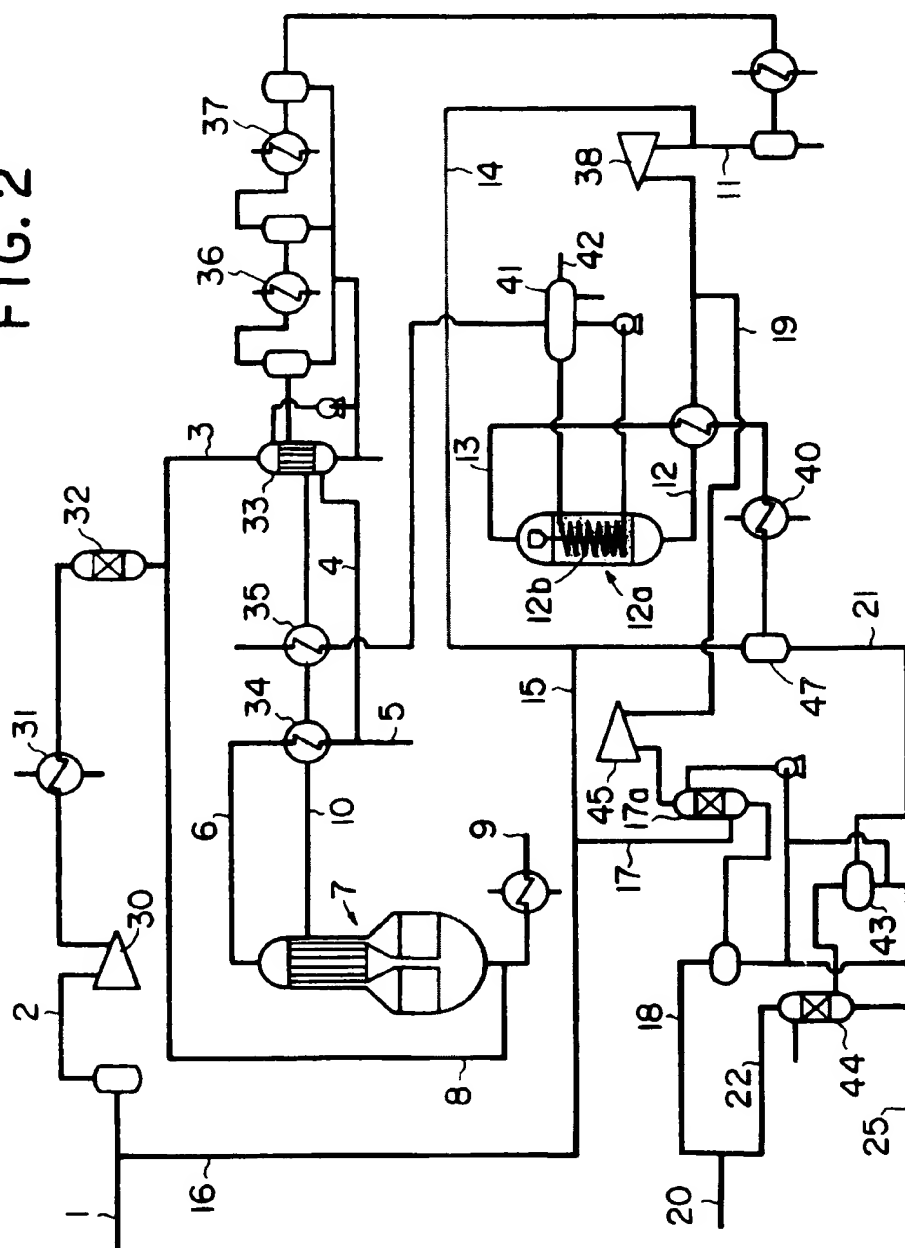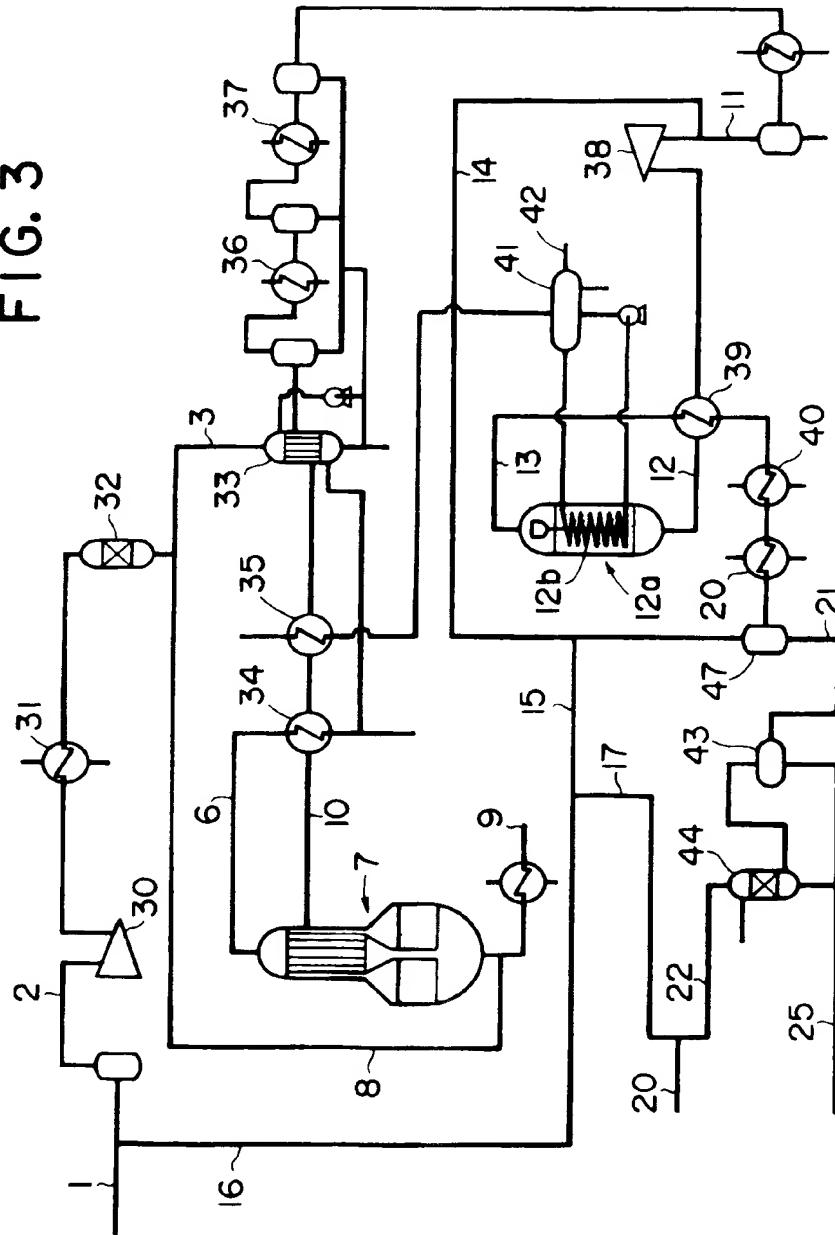
FIG.1

FIG. 2

FIG. 3

FIG. 4